
CHEMICAL ENGINEERING KINETICS

Third Edition

J. M. Smith

*Professor of Chemical Engineering
University of California at Davis*

McGraw-Hill Book Company

New York St. Louis San Francisco Auckland Bogotá Hamburg
Johannesburg London Madrid Mexico Montreal New Delhi
Panama Paris São Paulo Singapore Sydney Tokyo Toronto

This book was set in Times Roman.
The editor was Julianne V. Brown;
the production supervisor was Donna Pilgrá.
R. R. Donnelley & Sons Company was printer and binder.

CHEMICAL ENGINEERING KINETICS

Copyright © 1981, 1970, 1956 by McGraw-Hill, Inc. All rights reserved.
Printed in the United States of America. No part of this publication
may be reproduced, stored in a retrieval system, or transmitted, in any
form or by any means, electronic, mechanical, photocopying, recording, or
otherwise, without the prior written permission of the publisher.

890DODO89876

Library of Congress Cataloging in Publication Data

Smith, Joe Mauk, date

Chemical engineering kinetics.

(McGraw-Hill chemical engineering series)

Includes bibliographical references and index.

1. Chemical engineering. 2. Chemical reaction,

Rate of. 3. Thermodynamics. I. Title.

TP149.S58 1981 660.2'994 80-16486

ISBN 0-07-058710-8

Preface to the Third Edition	xiii
Preface to the Second Edition	xv
List of Symbols	xvii
1 Introduction	1
1-1 Interpretation of Rate Data, Scale-up, and Design	3
1-2 Chemical Kinetics	6
1-3 Kinetics and Thermodynamics	7
1-4 Thermodynamics of Chemical Reactions	9
1-5 Classification of Reactors	25
Bibliography	32
Problems	33
2 Chemical Kinetics	37
2-1 Rate of Homogeneous Reactions	38
2-2 Fundamentals of Rate Equations—Effect of Concentration	39
RATE EQUATIONS FROM PROPOSED MECHANISMS	41
2-3 Rate-Controlling Step	42
2-4 Stationary-State Approximation	43
2-5 Effect of Temperature—Arrhenius Equation	44
2-6 Prediction of Reaction Rates—Theories of Kinetics	51
2-7 Rate and Equilibrium Constants	55
2-8 Chain Reactions	57
EVALUATION OF RATE EQUATIONS FROM LABORATORY DATA	61
2-9 Concentration-vs.-Time Equations for Single, Irreversible Reactions	62
2-10 Concentrations-vs.-Time Equations for Reversible Reactions	71
ANALYSIS OF COMPLEX RATE EQUATIONS	82
2-11 First-Order Complex Reactions	84
2-12 Precision of Kinetics Measurements	90
Bibliography	91
Problems	92
	vii

3	Design Fundamentals and Mass Conservation Equations for Ideal Reactors	100
3-1	Reactor Design	101
3-2	Conservation of Mass in Reactors	104
3-3	The Ideal Stirred-Tank Reactor	107
3-4	The Ideal Tubular-Flow (Plug-Flow) Reactor	111
3-5	Deviations from Ideal Reactors	116
3-6	Space Velocity	118
3-7	Temperature Effects	121
3-8	Mechanical Features	122
	Problems	126
4	Isothermal Reactors for Homogeneous Reactions	130
4-1	Design Procedure—Batch Reactors	131
4-2	Rate Equations from Batch-Reactor Measurements; Total Pressure Method for Gaseous Reactions	136
4-3	Interpretation of Data from Laboratory Tubular-Flow Reactors	138
4-4	Design Procedure (Tubular-Flow Reactors)	158
4-5	Single Stirred-Tank Reactors	171
4-6	Stirred-Tank Reactors in Series	180
4-7	Comparison of Stirred-Tank and Tubular-Flow Reactors	182
4-8	Non-Steady Flow (Semibatch) Reactors	191
4-9	Batch-Recycle Reactors	199
4-10	Flow-Recycle Reactors	202
	Problems	205
5	Nonisothermal Reactors	217
5-1	Energy Conservation Equations	221
5-2	Batch, Stirred-Tank Reactors	222
5-3	Tubular-Flow Reactors	228
5-4	Continuous Stirred-Tank Reactors	242
5-5	Stable Operating Conditions in Stirred-Tank Reactors	246
5-6	Semibatch Reactors	251
5-7	Optimum Temperature Profiles	258
	Problems	263
6	Deviation from Ideal-Reactor Performance	268
6-1	Mixing Concepts and Models	268
6-2	A Residence-Time Distribution Function	270
6-3	Residence-Time Distributions from Response Measurements	271
6-4	Residence-Time Distributions for Reactors with Known Mixing Conditions	275
6-5	Interpretation of Response Data by the Dispersion Model	279
6-6	Interpretation of Response Data by the Series-of-Stirred-Tanks Model	282
6-7	Conversion in Nonideal Reactors	285
6-8	Conversion According to the Segregated-Flow Model	286
6-9	Conversion According to the Dispersion Model	288
6-10	Conversion According to the Series-of-Stirred-Tanks Model	290
6-11	Conversion According to the Recycle-Reactor Model	291
	Problems	294

ation	100	7 Heterogeneous Processes, Catalysis, and Adsorption	298
	101	HETEROGENEOUS PROCESSES	298
	104	7-1 Global Rates of Reaction	299
	107	7-2 Types of Heterogeneous Reactions	304
	111	CATALYSIS	306
	116	7-3 The Nature of Catalytic Reactions	306
	118	7-4 The Mechanism of Catalytic Reactions	309
	121	ADSORPTION	310
	122	7-5 Surface Chemistry and Adsorption	310
	126	7-6 Adsorption Isotherms	314
Reactions	130	7-7 Rates of Adsorption	320
	131	Problems	322
otal Pressure	136	8 Solid Catalysts	327
Reactors	138	8-1 Determination of Surface Area	329
	158	8-2 Void Volume and Solid Density	334
	171	8-3 Pore-Volume Distribution	338
	180	8-4 Theories of Heterogeneous Catalysis	348
	182	8-5 Classification of Catalysts	350
ors	191	8-6 Catalyst Preparation	351
	199	8-7 Promoters and Inhibitors	353
	202	8-8 Catalyst Deactivation (Poisoning)	354
	205	Problems	356
	217	9 Rate Equations for Fluid-Solid	
	221	Catalytic Reactions	359
	222	9-1 Rates of Adsorption, Desorption, Surface Reaction	360
	228	9-2 Rate Equations in terms of Fluid-Phase Concentrations	
	242	at the Catalyst Surface	363
	246	9-3 Qualitative Analysis of Rate Equations	367
	251	9-4 Quantitative Interpretation of Kinetics Data	371
	258	9-5 Redox Rate Equations	375
	263	9-6 Kinetics of Catalyst Deactivation	381
nce	268	Problems	383
	268		
ements	270	10 External Transport Processes in	
wn Mixing	271	Heterogeneous Reactions	389
	275	FIXED-BED REACTORS	390
odel	279	10-1 The Effect of Physical Processes on Observed Rates of Reaction	392
red-Tanks Model	282	10-2 Mass- and Heat-Transfer Coefficients (Fluid-Particle) in Packed Beds	394
	285	10-3 Quantitative Treatment of External Transport Effects	398
	286	10-4 Stable Operating Conditions	406
	288	10-5 Effect of External Transport Processes on Selectivity	408
Model	290	FLUIDIZED-BED REACTORS	412
	291		
	294	10-6 Particle-Fluid Mass and Heat Transfer	413

SLURRY REACTORS		415
10-7	Mass-Transfer Coefficients: Gas Bubble to Liquid (k_L)	419
10-8	Mass-Transfer Coefficients: Liquid to Particle (k_c)	425
10-9	The Effect of Mass Transfer on Observed Rates	430
TRICKLE-BED REACTORS		434
10-10	Mass-Transfer Coefficients: Gas to Liquid ($k_L a_g$)	436
10-11	Mass-Transfer Coefficients: Liquid to Particle (k_c, a_c)	437
10-12	Calculation of Global Rate Problems	437
		442
11 Internal Transport Processes—Reaction and Diffusion in Porous Catalysts		450
INTRAPELLET MASS TRANSFER		451
11-1	Gaseous Diffusion in Single Cylindrical Pores	452
11-2	Diffusion in Liquids	461
11-3	Diffusion in Porous Catalysts	462
11-4	Surface Diffusion	470
INTRAPELLET HEAT TRANSFER		473
11-5	Concept of Effective Thermal Conductivity	473
11-6	Effective Thermal-Conductivity Data	474
MASS TRANSFER WITH REACTION		477
11-7	Effectiveness Factors	478
11-8	The Significance of Intrapellet Diffusion: Evaluation of the Effectiveness Factor	483
11-9	Experimental and Calculated Effectiveness Factors	491
11-10	The Effect of Intrapellet Mass Transfer on Observed Kinetics	494
MASS AND HEAT TRANSFER WITH REACTION		500
11-11	Nonisothermal Effectiveness Factors	500
11-12	Experimental Nonisothermal Effectiveness Factors	503
EFFECT OF INTERNAL TRANSPORT ON SELECTIVITY AND POISONING		507
11-13	Selectivities for Porous Catalysts	507
11-14	Rates for Poisoned Porous Catalysts Problems	512
		517
12 Laboratory Reactors—Interpretation of Experimental Data		522
12-1	Interpretation of Laboratory Kinetics Data	523
12-2	Homogeneous Laboratory Reactors	532
12-3	Heterogeneous Laboratory Reactors	535
12-4	Calculation of the Global Rate	537
12-5	The Structure of Reactor Design Problems	541
		545

415	13 Design of Heterogeneous Catalytic Reactors	548
419	FIXED-BED REACTORS	549
425	13-1 Construction and Operation	549
430	13-2 Outline of the Design Problem	552
434	ISOTHERMAL AND ADIABATIC FIXED-BED REACTORS	554
436	13-3 Isothermal Operation	554
437	13-4 Adiabatic Operation	563
442	NONISOTHERMAL, NONADIABATIC FIXED-BED REACTORS	568
	13-5 The One-Dimensional Model	569
	13-6 The Two-Dimensional Model	582
450	13-7 Dynamic Behavior	593
	13-8 Variations of Fixed-Bed Reactors	594
451	13-9 Importance of Transport Processes in Fixed-Bed Reactors	598
452	FLUIDIZED-BED REACTORS	599
461	13-10 Two-Phase, Fluidized-Bed Model	601
462	13-11 Operating Characteristics	604
470	SLURRY REACTORS	606
473	13-12 Slurry Reactor Models	607
473	TRICKLE-BED REACTORS	614
474	13-13 Trickle-Bed Reactor Model	615
477	OPTIMIZATION	626
478	Problems	628
483	14 Fluid-Solid Noncatalytic Reactions	636
491	14-1 Design Concepts	637
494	SINGLE PARTICLE BEHAVIOR	638
500	14-2 Kinetics and Mass Transfer	638
503	14-3 The Global Rate (Shrinking-Core Model)	642
	REACTOR MODELS	645
507	14-4 Conversion vs. Time for Single Particles (Constant Fluid Concentration)	645
507	14-5 Conversion in Reactors with Constant Fluid Concentration	648
512	14-6 Conversion for Variable Fluid Composition	655
517	Problems	661
	Indexes	665
522	Author Index	
523	Subject Index	
532		
535		
537		
541		
545		

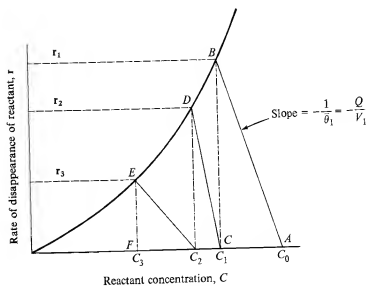
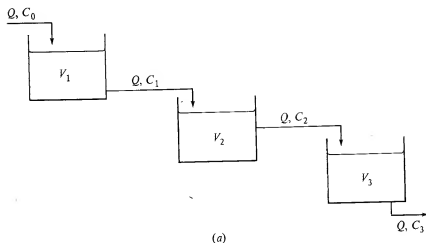
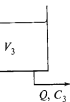


Figure 4-14 (a) Steady operation of three stirred-tank reactors in series. (b) Graphical solution for stirred-tank reactors in series.

4-7 Comparison of Stirred-Tank and Tubular-Flow Reactors

The stirred-tank reactor has certain advantages because of the uniform temperature, pressure, and composition attained as a result of mixing. As mentioned, it is possible to operate such a reactor under isothermal conditions even when the heat of reaction is high—an impossibility in the usual tubular type. When a small temperature variation is desired, for example, to minimize side reactions or avoid unfavorable rates, the opportunity for isothermal operation at the optimum temperature is a distinct advantage. Stirred-tank reactors, by virtue of their large



volumes (and hence their large V/F values) provide a long residence time. This, combined with the isothermal nature of the reactor, permits operation at the optimum temperature for a long reaction time. For rate equations of certain types the selectivity in multiple reactions may be greater in tank reactors than in tubular-flow reactors for the same residence time. For other forms of the rate equations the reverse is true. Examples later in this section illustrate this point.

For high-pressure reactions it is usually necessary, because of cost considerations, to use small-diameter tubular reactors rather than tank types. Tank reactors that are to be operated at high pressures require a large wall thickness and complex sealing arrangements for the mixer shaft, factors which increase both initial and maintenance costs. Stirred-tank performance may be achieved in a recycle form of tubular-flow reactor, as illustrated in Fig. 1-7a. The diameter may be minimized for high-pressure operation by constructing the reactor in the form of a closed loop of tubing with entrance and exit connections and with a recycle pump in the loop.[†]

The rate of heat transfer per unit mass of reaction mixture is generally lower in the conventional tank type than in a small-diameter tubular reactor, chiefly because of the lower ratio of surface area (available for heat transfer) to volume in the tank reactors and their lower heat-transfer coefficients. So, in instances where the heat of reaction is high it may be desirable to use a tubular reactor. For example, various thermal reactions of hydrocarbons require significant amounts of thermal energy at an elevated temperature level. This would be difficult to accomplish with a large-diameter reactor because of the limited external heat-transfer surface (per unit mass of reaction mixture) and the low coefficient of heat transfer from the oil in the tank to the tank wall. In the tubular reactors (pipe stills) used in industry the coefficient of heat transfer can be increased by forcing the oil through the tubes at a high speed. It is also apparent that severe difficulties would arise in attempting to provide for efficient stirring under reaction conditions (800 to 1200°F, 300 to 800 lb/in.² abs). The tubular-loop reactor operated at high circulation rates can give complete mixing in a small-diameter tube and high rates of heat transfer. By introducing small solid particles that are free to move, a type is obtained in which there is considerable mixing. Such fluidized-bed reactors also give improved heat-transfer coefficients between the fluid and the wall.

In summary, stirred-tank reactors have been employed on a commercial scale mainly for liquid-phase reaction systems at low or medium pressures. Stirred-tank reactors can be used when the heat of reaction is high, but only if the temperature level obtained in their isothermal operation is satisfactory from other standpoints. If the reactions are endothermic and a high temperature is required, tubular reactors are usually indicated. However, a tank type may be employed as a semibatch unit for a highly exothermic reaction. For example, the production of hexamethylenetetramine by reacting ammonia and formaldehyde (in aqueous solution) is highly exothermic, but the rate of reaction is rapid and 100% conversion is possible over a range of temperature of at least 80 to 100°C. By adjusting

[†] Practical advantages of loop reactors are discussed in *Process Engineering*, p. 62, December 1973 and *Hydrocarbon Processing*, 55, 99 (June 1976).

(b) Graphical solution for

reactors

of the uniform temperature. As mentioned, it is possible even when the heat of reaction is high to use a tank type. When a small-diameter tubular reactor is used, side reactions or avoidances can be minimized at the optimum temperature by virtue of their large

the rate of feed and reactor volume, it is possible to add the feed at 20°C and remove enough heat to keep the reaction mixture below 100°C.

Denbigh and coworkers[†] have discussed the technical advantages and disadvantages of continuous-stirred-tank reactors, especially in comparison with batch-operated tank reactors. Stead, Page, and Denbigh[‡] describe experimental techniques for evaluating rate equations from stirred-tank data. Rase[§] presents practical and technical aspects of both plug-flow and stirred-tank reactors.

In stirred-tank equipment the reaction occurs at a rate determined by the composition of the exit stream from the reactor. Since the rate generally decreases with the extent of conversion, the tank reactor operates at the lowest point in the range between the high rate corresponding to the composition in the reactor feed and the low rate corresponding to the exit composition. In the tubular type maximum advantage is taken of the high rates corresponding to low conversions in the first part of the reactor. This means that the tank reactor must have a larger volume for a given feed rate (larger V/F value). Of course, this reasoning does not take into account the effects of side reactions or temperature variations; these may offset this disadvantage of the tank reactor, as illustrated in Example 5-3. Also, the total volume required in a tank-flow reactor can be reduced by using several small units in series. The relation between volumes required in stirred-tank and tubular-flow reactors can be illustrated by reference to a constant volume first-order reaction. Equation (3-5) is applicable for the stirred-tank reactor and gives

$$\frac{V_s}{Q} = \frac{C_0 - C}{r} = \frac{C_0 - C}{kC}$$

where C refers to the concentration of reactant and r to its rate of disappearance. In terms of conversion of reactants

$$x = \frac{C_0 - C}{C_0} = \frac{k(V_s/Q)}{1 + k(V_s/Q)} \quad (4-17)$$

For the tubular-flow case Eq. (3-18) can be used:

$$\frac{V_F}{Q} = C_0 \int \frac{dx}{r} = C_0 \int_0^x \frac{dx}{kC_0(1-x)} = \frac{-1}{k} \ln(1-x)$$

or

$$x = 1 - e^{-k(V_F/Q)} \quad (4-18)$$

Equations (4-17) and (4-18) are plotted in Fig. 4-15 as conversion vs. $k(V/Q)$. For equal flow rates $k(V/Q)$ is proportional to the volume. It is clear that for any conversion the volume required is largest for the tank reactor and that the difference increases with residence time. We can obtain a direct measure of the ratio of

[†] K. G. Denbigh, *Trans. Faraday Soc.*, **40**, 352 (1944), **43**, 648 (1947); K. G. Denbigh, M. Hicks, and F. M. Page, *Trans. Faraday Soc.*, **44**, 479 (1948).

[‡] B. Stead, F. M. Page, and K. G. Denbigh, *Disc. Faraday Soc.*, **2**, 263 (1947).

[§] H. F. Rase, "Chemical Reactor Design for Process Plants," chap. 6, John Wiley & Sons, New York, 1977.

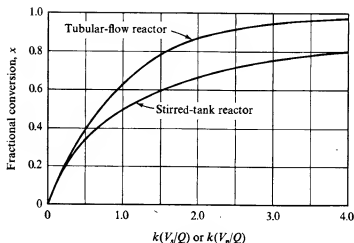


Figure 4-15 Conversion in stirred-tank and plug-flow reactors.

volume V_s of the stirred-tank reactor to volume V_p of the tubular-flow (plug-flow) reactor at the same conversion by equating Eqs. (4-17) and (4-18).

$$\frac{k(V_s/Q)}{1 + k(V_s/Q)} = 1 - e^{-k(V_p/Q)}$$

If α is the ratio of volumes, $\alpha = V_s/V_p$, then the previous equation can be written in terms of V_p and α .

$$\frac{\alpha k(V_p/Q)}{1 + \alpha k(V_p/Q)} = 1 - e^{-k(V_p/Q)} \quad (4-19)$$

If we now replace $k(V_p/Q)$ in Eq. (4-19) with the function of x from Eq. (4-18) and solve for α , we have the ratio of volumes as a function of conversion,

$$\alpha = \frac{x}{(x-1) \ln(1-x)} \quad (4-20)$$

This result is plotted in Fig. 4-16 and shows that at low conversions there is little to be gained in using a tubular-flow reactor, but at conversions of 70% or larger more than twice as much volume is required for a stirred-tank unit.[†]

Selectivity may also be different in stirred-tank and tubular-flow reactors. It has been shown[‡] that, depending on the kinetics and nature of the multiple reactions, selectivity obtained in a stirred-tank reactor may be less, the same as, or greater than that for a tubular-flow reactor. Examples of reaction systems for each result are given in Table 4-12. The order of the rate equation is assumed to follow the stoichiometry for each reaction. Since the stirred-tank reactor corresponds to

[†] Reactor volume vs. conversion for other forms of rate equations and for different reactor types is given by Wirges and Shah, *Hydrocarbon Processing*, 55, (April 1976).

[‡] T. E. Corrigan, G. A. Lessells, and M. J. Dean, *Ind. Eng. Chem.*, 60, 62 (1968).

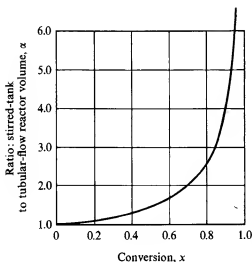


Figure 4-16 Ratio of volumes required for stirred-tank and tubular-flow (plug-flow) reactors.

complete mixing and the tubular-flow unit to no axial mixing, the table shows the effect of mixing upon selectivity. The following example illustrates the method of establishing the conclusions given in Table 4-12.

Example 4-12 Develop equations for the selectivity of product *B* with respect to *D* for reaction system 1 of Table 4-12 for stirred-tank and tubular-flow reactors. Assume isothermal conditions and constant density. Let capital letters designate concentrations. In the feed $A = A_0$ and $B = D = 0$.

SOLUTION The reaction sequence is



Table 4-12 Effect of mixing on selectivity for various types of reaction systems

Reaction system	Reaction type	Overall selectivity†
1. $A \rightarrow B$ $B \rightarrow D$	Consecutive (first order)	$S_S < S_p$ (selectivity of <i>B</i> with respect to <i>D</i>)
2. $A + B \rightarrow R$ $A + R \rightarrow S$	Consecutive (second order)	$S_S < S_p$ (selectivity of <i>R</i> with respect to <i>S</i>)
3. $A \rightarrow B$ $A \rightarrow C$	Parallel (equal, first order)	$S_p = S_S$ (selectivity of <i>B</i> with respect to <i>C</i>)
4. $A + B \rightarrow C$ $A + B \rightarrow D$	Parallel (equal, second order)	$S_p = S_S$ (selectivity of <i>C</i> with respect to <i>D</i>)
5. $A + B \rightarrow C$ $2A \rightarrow D$	Parallel (unequal order with respect to <i>A</i>)	$S_S > S_p$ (selectivity of <i>C</i> with respect to <i>D</i>)

† Selectivity, as defined in Chap. 2, is the ratio of the yield of one product to that of another.

In Sec. 2-11 this system was analyzed for a constant-volume batch reactor. Since the tubular-flow reactor will have the same form of mass balance (see Sec. 3-4) as that for the batch reactor the results in Sec. 2-11 can be applied here if t is replaced with the residence time V/Q . Hence the overall selectivity for a tubular-flow reactor is given by the ratio of Eqs. (2-89) and (2-90). Since $A/A_0 = 1 - x_r$, this ratio is

$$S_p = \frac{x_B}{x_D} = \frac{[k_1/(k_1 - k_3)][(1 - x_r)^{k_3/k_1} - (1 - x_r)]}{[k_1/(k_1 - k_3)][1 - (1 - x_r)^{k_3/k_1}] - [k_3/(k_1 - k_3)]x_r} \quad (A)$$

For the stirred-tank case Eq. (3-5) may be written for components A , B , and D † as follows:

$$\bar{\theta} = \frac{V}{Q} = \frac{A_0 - A}{k_1 A} \quad \text{or} \quad A = \frac{A_0}{1 + k_1 \bar{\theta}} \quad (B)$$

$$\bar{\theta} = \frac{V}{Q} = \frac{0 - B}{k_3 B - k_1 A} \quad \text{or} \quad B = \frac{k_1 \bar{\theta} A}{1 + k_3 \bar{\theta}} \quad (C)$$

$$\bar{\theta} = \frac{V}{Q} = \frac{0 - D}{-k_3 B} \quad \text{or} \quad D = k_3 \bar{\theta} B \quad (D)$$

From Eqs. (B) and (C),

$$\frac{B}{A_0} = x_B = \frac{k_1 \bar{\theta}}{(1 + k_1 \bar{\theta})(1 + k_3 \bar{\theta})} \quad (E)$$

Using this result in Eq. (D) gives

$$\frac{D}{A_0} = x_D = \frac{k_1 \bar{\theta} k_3 \bar{\theta}}{(1 + k_1 \bar{\theta})(1 + k_3 \bar{\theta})} \quad (F)$$

Then the selectivity S_s in the stirred-tank reactor will be

$$S_s = \frac{x_B}{x_D} = \frac{1}{k_3 \bar{\theta}} \quad (G)$$

This result may be expressed in terms of the total conversion of A by noting, from Eq. (B), that

$$k_1 \bar{\theta} = \frac{A_0}{A} - 1 = \frac{x_r}{1 - x_r}$$

Using this result in Eq. (G) to eliminate $\bar{\theta}$ gives

$$S_s = \frac{k_1}{k_3} \frac{1 - x_r}{x_r} \quad (H)$$

Equations (A) and (H) can be employed to calculate S_p and S_s for any conversion. The results are shown in Fig. 4-17 for $k_1/k_3 = 2$. The relative position of

† Alternately, mass balance equations could be written for each reaction and a specific component, and then a total mass balance used to obtain the three required equations (See Examples 4-7, 4-9).

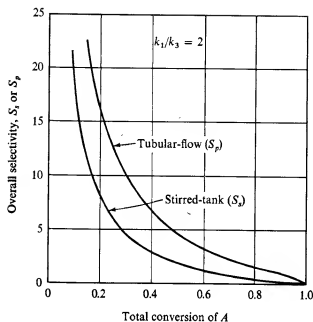


Figure 4-17 Selectivity for consecutive reactions in stirred-tank and tubular-flow reactors.

the two curves would be the same for other values of k_1/k_3 . Note that the selectivity of B with respect to D is greater in the tubular-flow reactor for all conversions, although the difference approaches zero as the conversion approaches zero.

Table 4-12 compares selectivities for *single* reactors. For some reaction systems a combination of stirred-tank and tubular-flow units may give higher selectivities than a single reactor of the same total volume. The possible combinations of number and arrangement of reactors and reaction systems are huge. However, the approach to selectivity evaluation is the same and follows the methods described in Example 4-12. A simple illustration of the conversion obtained in a combination of reactors is given in the following example.

Example 4-13 A dilute aqueous solution of acetic anhydride is to be hydrolyzed continuously at 25°C. At this temperature the rate equation for the disappearance of anhydride is

$$r = 0.158C, \text{ g mol}/(\text{cm}^3)(\text{min})$$

where C is the concentration of anhydride, in gram moles per cubic centimeter. The feed rate to be treated is $500 \text{ cm}^3/\text{min}$ of solution, with an anhydride concentration of $1.5 \times 10^{-4} \text{ g mol}/\text{cm}^3$.

There are two 2.5-liter and one 5-liter reaction vessels available, with excellent agitation devices.

- (a) Would the conversion be greater if the one 5-liter vessel were used as a steady-flow tank reactor or if the two 2.5-liter vessels were used as reac-

- tors in series? In the latter case all the feed would be sent to the first reactor and the product from that would be the feed to the second reactor.
- Would a higher conversion be obtained if the two 2.5-liter vessels were operated in parallel; that is, if $250 \text{ cm}^3/\text{min}$ of feed were fed to each reactor and then the effluent streams from each reactor joined to form the final product?
 - Compare the conversions calculated in parts (a) and (b) with that obtainable in a tubular-flow reactor of 5-liter volume.
 - Would the conversion be increased if a tank-flow reactor of 2.5 liters were followed with a 2.5-liter tubular-flow reactor?

Assume that the density of the solutions is independent of concentrations and that operation is steady state.

SOLUTION Since this is a first-order constant-density reaction, Eqs. (4-17) and (4-18) give the conversions for single-stirred-tank and ideal tubular-flow reactors in terms of residence time V/Q . For multiple-stirred-tank reactors Eq. (A) of Example (4-11) is applicable.

(a) For a single 5-liter vessel, $\bar{\theta} = 5000/500 = 10 \text{ min}$. From Eq. (4-17),

$$x = \frac{0.158(10)}{1 + 0.158(10)} = 0.612$$

For two 2.5-liter reactors in series,

$$\bar{\theta}_1 = \bar{\theta}_2 = \frac{2,500}{500} = 5 \text{ min}$$

Substituting in Eq. (A) of Example 4-11 gives

$$x = 1 - \frac{1}{(1 + k\bar{\theta})^2} = 1 - \frac{1}{[1 + 0.158(5)]^2} = 0.688$$

- For a 2.5-liter reactor with a feed rate of $250 \text{ cm}^3/\text{min}$, $\bar{\theta} = 10 \text{ min}$. Hence the conversion will be the same as for the 5-liter reactor with $Q = 500 \text{ cm}^3/\text{min}$, that is, 0.612.
- For a single tubular-flow reactor, from Eq. (4-18),

$$x = 1 - e^{-0.158(5000/500)} = 1 - 0.206 = 0.794$$

- In the first reactor, $\bar{\theta}_1 = 2500/500 = 5 \text{ min}$. Hence the conversion in the product stream from the first reactor will be

$$x_1 = \frac{k\bar{\theta}_1}{1 + k\bar{\theta}_1} = \frac{0.158(5)}{1 + 0.158(5)} = 0.442$$

When the conversion in the feed stream to a tubular-flow reactor is x_1 rather than zero, integration of Eq. (3-18) gives

$$\theta = C_0 \int_{x_1}^{x_2} \frac{dx}{r} = C_0 \int_{x_1}^{x_2} \frac{dx}{kC_0(1-x)} = -\frac{1}{k} [\ln(1-x_2) - \ln(1-x_1)]$$

or

$$x_2 = 1 - (1 - x_1)e^{-k\theta}$$

Table 4-13

Type	Conversion, %
Single-stirred tank (5 liters)	61.2
Two stirred tanks in parallel (each 2.5 liters)	61.2
Two stirred tanks in series (each 2.5 liters)	68.8
Stirred tank followed by tubular- flow reactor (each 2.5 liters)	74.6
Single tubular-flow reactor (5 liters)	79.4

The residence time in the second tubular-flow reactor is also 5 min. With a feed of conversion $x_1 = 0.442$, the final conversion would be

$$x_2 = 1 - (1 - 0.442)e^{-0.158(5)} = 1 - 0.254 = 0.746$$

The various results, arranged in order of increasing conversion, are shown in Table 4-13.

In the previous example increasing the number of stirred-tank reactors from one to two (with the same total residence time) caused an increase in conversion from 61.2% to 68.8%. Further increase in number of tank reactors in series would lead to a maximum conversion of 79.4%, the value for a tubular-flow reactor with the same residence time. An infinite number of stirred-tank reactors in series is equivalent to a tubular-flow reactor, provided the total residence time is the same. This may be demonstrated by deriving Eq. (4-18) from Eq. (A) of Example 4-11, which is applicable for equal residence time in each stirred tank. For a total residence time of $\bar{\theta}$, Eq. (A) becomes

$$x = 1 - \frac{1}{(1 + k\bar{\theta}/n)^n} \quad (4-21)$$

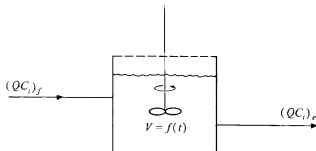


Figure 4-18 Semibatch reactor (stirred-tank type).

It is known that

$$\lim_{n \rightarrow \infty} \left(1 + \frac{\alpha}{n}\right)^n = e^\alpha$$

If we use this result with $\alpha = k\bar{t}$, Eq. (4-21) becomes

$$x = 1 - e^{-k\bar{t}}$$

which is the same as Eq. (4-18).

4-8 Non-Steady Flow (Semibatch) Reactors

A tank-type reactor which does not operate at steady-state can be described as a semibatch reactor. Semibatch behavior occurs when a tank-flow reactor is started up, when its operating conditions are changed from one steady state to another, or when it is shut down. Purging processes in which an inert material is added to the reactor can also be classified as semibatch operation.

In addition to applications arising from short-period deviations from steady-state, the semibatch reactor often is used for its own particular characteristics. For example, it is sometimes advantageous to add all of one reactant initially and then add the other reactant continuously. When the heat of reaction is large, the energy evolution can be controlled by regulating the rate of addition of one of the reactants. In this way limited heat-transfer characteristics of tank reactors can be partially eliminated. This form of operation also allows for a degree of control of concentration of the reaction mixture, and hence rate of reaction, that is not possible in batch or continuous-flow reactors. Another example is the case in which the reactants are all added initially to the vessel but one of the products is removed continuously, as in the removal of water by boiling in esterification reactions. The advantage here is an increase in rate, owing to the removal of one of the products of a reversible reaction and to increased concentrations of reactants.

The mass-balance equations for semibatch operation (illustrated in Fig. 4-18) may include all four of the terms in the general balance, Eq. (3-1). The feed and withdrawal streams can cause changes in composition and volume of the mixture in the reactor, in addition to such changes due to the reaction itself. Many operating alternatives exist. One reactant may be present in the initial charge to the reactor and the second reactant added continuously, periodically, or at a continuously varying rate. Similarly, product can be removed in a variety of ways. After presenting general equations, semibatch reactor problems will be illustrated with two special cases (Examples 4-14 and 4-15).

In terms of the molal concentration C_i of species i , volumetric flow rate Q , reactor volume V , Eq. (3-1) takes the form:

$$(QC_i)_f - (QC_i)_r + r_i V = \frac{d[V(C_i)]}{dt} \quad (4-22)^\dagger$$

[†] Note that C_i and r_i in the reactor are equal to their values in the effluent stream for an ideal stirred tank. Also note that Eq. (4-22) reduces to the usual form for a batch reactor [Eq. (3-2)]_b, if there are no feed or effluent streams, and to Eq. (3-4) for a continuous-flow steady-state reactor.